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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B05D 7/24, D06M 10/02, 14/18, 10/08, 10/10	A1	(11) International Publication Number: WO 00/20130 (43) International Publication Date: 13 April 2000 (13.04.00)
(21) International Application Number: PCT/GB99/03224 (22) International Filing Date: 29 September 1999 (29.09.99) (30) Priority Data: 9821267.3 1 October 1998 (01.10.98) GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency Ively Road, Farnborough, Hampshire GU14 0LX (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): WILLIS, Colin, Robert [GB/GB]; CBD Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). BREWER, Stuart, Anson [GB/GB]; CBD Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). BADYAL, Jas, Pal, Singh [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). COULSON, Stephen, Richard [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). (74) Agent: BOWDERY, A., O.; D/IPR, Formalities Section (DERA), Poplar 2, MOD Abbey Wood #19, Bristol BS34 8JH (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: SURFACE COATINGS		
(57) Abstract A method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising an optionally substituted alkyne so as to form an oil or water repellent coating on said substrate. Suitable compounds for use in the methods are compounds of formula (I) $R^4-C\equiv C-X-R^5$ where R^4 is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl optionally substituted by halo; X is a bond or a bridging group; and R^5 is an alkyl, cycloalkyl or aryl group optionally substituted by halogen. The method is particularly useful in the production of oil and/or water repellent fabrics.		

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Surface Coatings

The present invention relates to the coating of surfaces, in particular to the production of oil- and water- repellent surfaces, as well as to coated articles obtained thereby.

Oil- and water- repellent treatments for a wide variety of surfaces are in widespread use. For example, it may be desirable to impart such properties to solid surfaces, such as metal, glass, ceramics, paper, polymers etc. in order to improve preservation properties, or to prevent or inhibit soiling.

A particular substrate which requires such coatings are fabrics, in particular for outdoor clothing applications, sportswear, leisurewear and in military applications. Their treatments generally require the incorporation of a fluoropolymer into or more particularly, fixed onto the surface of the clothing fabric. The degree of oil and water repellency is a function of the number and length of fluorocarbon groups or moieties that can be fitted into the available space. The greater the concentration of such moieties, the greater the repellency of the finish.

25

In addition however, the polymeric compounds must be able to form durable bonds with the substrate. Oil- and water- repellent textile treatments are generally based on fluoropolymers that are applied to fabric in the form of an aqueous emulsion. The fabric remains breathable and permeable to air since the treatment simply coats the fibres with a very thin, liquid-repellent film. In order to make these finishes durable, they are sometimes co-applied with cross-linking resins that bind the fluoropolymer treatment

to fibres. Whilst good levels of durability towards
laundering and dry-cleaning can be achieved in this way, the
cross-linking resins can seriously damage cellulosic fibres
5 and reduce the mechanical strength of the material.
Chemical methods for producing oil- and water-repellent
textiles are disclosed for example in WO 97/13024 and
British patent No 1,102,903 or M. Lewin et al., 'Handbook of
Fibre Science and Technology' Marcel and Dekker Inc., New
10 York, (1984) Vol 2, Part B Chapter 2.

Plasma deposition techniques have been quite widely used for
the deposition of polymeric coatings onto a range of
surfaces. This technique is recognised as being a clean,
15 dry technique that generates little waste compared to
conventional wet chemical methods. Using this method,
plasmas are generated from small organic molecules, which
are subjected to an ionising electrical field under low
pressure conditions. When this is done in the presence of a
20 substrate, the ions, radicals and excited molecules of the
compound in the plasma polymerise in the gas phase and react
with a growing polymer film on the substrate. Conventional
polymer synthesis tends to produce structures containing
repeat units which bear a strong resemblance to the monomer
25 species, whereas a polymer network generated using a plasma
can be extremely complex.

The success or otherwise of plasma polymerisation depends
upon a number of factors, including the nature of the
30 organic compound. Reactive oxygen containing compounds such
as maleic anhydride, have previously been subjected to
plasma polymerisation (Chem. Mater. Vol. 8, 1, 1996).

US Patent No 5,328,576 describes the treatment of fabric or paper surfaces to impart liquid repellent properties by subjecting the surfaces to a pre-treatment with an oxygen plasma, followed by plasma polymerisation of methane.

5

However, plasma polymerisation of the desirable oil and water repellent fluorocarbons have proved more difficult to achieve. It has been reported that cyclic fluorocarbons undergo plasma polymerisation more readily than their acyclic counterparts (H. Yasuda et al., J. Polym. Sci., Polym. Chem. Ed. 1977, 15, 2411). The plasma polymerization of trifluoromethyl-substituted perfluorocyclohexane monomers has been reported (A. M. Hynes et al., Macromolecules, 1996, 29, 18-21).

15

A process in which textiles are subjected to plasma discharge in the presence of an inert gas and subsequently exposed to an F-containing acrylic monomer is described in SU-1158-634. A similar process for the deposition of a fluoroalkyl acrylate resists on a solid substrate is described in European Patent Application No. 0049884.

20

Japanese application no. 816773 describes the plasma polymerisation of compounds including fluorosubstituted acrylates. In that process, a mixture of the fluorosubstituted acrylate compounds and an inert gas are subjected to a glow discharge.

25

The applicants have found an improved method of producing polymer and particular halopolymer coatings which are water and/or oil repellent on surfaces.

30

According to the present invention there is provided a method of coating a surface with a polymer layer, which

method comprises exposing said surface to a plasma comprising an optionally substituted alkyne so as to form an oil or water repellent coating on said substrate.

- 5 Suitably the alkyne compounds used in the method of the invention comprise chains of carbon atoms, including one or more carbon-carbon triple bonds. The chains may be optionally interposed with a heteroatom and may carry substituents including rings and other functional groups.
- 10 Suitable chains, which may be straight or branched, have from 2 to 50 carbon atoms, more suitably from 6 to 18 carbon atoms. They may be present either in the monomer used as a starting material, or may be created in the monomer on application of the plasma, for example by the ring opening
- 15 of an optionally substituted cycloalkyl group.

As used herein, the term "heteroatom" includes oxygen, sulphur, silicon or nitrogen atoms. Where a chain of carbon atoms is interposed by a nitrogen atom, it will be

20 substituted so as to form a secondary or tertiary amine. Similarly, silicons will be substituted appropriately, for example with two alkoxy groups.

Other terms used herein include "halo" or "halogen" which

25 refer to fluorine, chlorine, bromine and iodine. Particularly preferred halo groups are fluoro. The term "aryl" refers to aromatic cyclic groups such as phenyl or naphthyl, in particular phenyl. The term "alkyl" refers to straight or branched chains of carbon atoms, suitably of up

30 to 50 carbon atoms in length. Derivatives of alkyl groups, such as would be understood by "alkoxy" include such groups.

The term "heterocyclyl" includes aromatic and non aromatic rings or ring systems, suitably containing up to 12 atoms, up to three of which may be heteroatoms.

- 5 Suitable optional substituents for the alkynes used in the process of the invention include halo, cyano, nitro, oxo, epoxide, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted aralkyl, optionally substituted heterocyclyl, $C(O)_nR^1$, OR^1 , $S(O)_mR^1$, NR^2R^3 ,
 10 $C(O)NR^2R^3$, $OC(O)NR^2R^3$, $=NOR^2$, $-NR^2C(O)_nR^3$, $-NR^1CONR^2R^3$, $-N=CR^3R^3$, $S(O)_mNR^2R^3$ or $-NR^2S(O)_mR^1$ where R^1 , R^2 and R^3 are independently selected from hydrogen or alkyl, aralkyl, cycloalkyl, aryl or heterocyclyl, any of which may be optionally substituted, or R^2 and R^3 together form an optionally substituted ring
 15 which optionally contains further heteroatoms such as sulphur, oxygen and nitrogen, n is 1 or 2, m is 0, 1 or 2.

- Suitable optional substituents for aryl, aralkyl and cycloalkyl and heterocyclyl groups R^1 , R^2 and R^3 include
 20 halo, perhaloalkyl, mercapto, hydroxy, alkoxy, oxo, heteroaryloxy, alkenyloxy, alkynyloxy, alkoxyalkoxy, aryloxy (where the aryl group may be substituted by halo, nitro, or hydroxy), cyano, nitro, amino, mono- or di-alkyl amino, alkylamido or oximino.

25

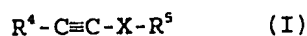
Suitable alkynyl chains, which may be straight or branched, have from 2 to 50 carbon atoms, more suitably from 6 to 20 carbon atoms, and preferably from 8 to 15 carbon atoms.

- 30 Monomeric compounds where the chains comprise unsubstituted alkynyl groups are suitable for producing coatings which are water repellent. By substituting at least some of the hydrogen atoms in these compounds with at least some

fluorine atoms, oil repellency may also be conferred by the coating.

Thus in a preferred aspect, the monomeric compounds include
5 haloalkyl moieties and in particular fluoroalkyl moieties.
Therefore, preferably the plasma used in the method of the
invention will comprise a monomeric unsaturated haloalkynyl
containing organic compound.

10 Particularly suitable monomeric organic compounds are those
of formula (I)



15 where R^4 is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl
optionally substituted by halo;
 X is a bond or a bridging group; and
 R^5 is an alkyl, cycloalkyl or aryl group optionally
substituted by halogen.

20

Suitable bridging groups X include groups of formulae
- $(CH_2)_s$ -, - $CO_2(CH_2)_p$ -, - $(CH_2)_pO(CH_2)_q$ -, - $(CH_2)_pN(R^6)CH_2)_q$ -,
- $(CH_2)_pN(R^6)SO_2$ -, where s is 0 or an integer of from 1 to 20,
 p and q are independently selected from integers of from 1
25 to 20; and R^6 is hydrogen, alkyl, cycloalkyl or aryl.
Particular alkyl groups for R^6 include C_{1-6} alkyl, in
particular, methyl or ethyl.

Where R^4 is alkyl or haloalkyl, it is generally preferred to
30 have from 1 to 6 carbon atoms.

Suitable haloalkyl groups for R^4 include fluoroalkyl groups.
The alkyl chains may be straight or branched and may include
cyclic moieties.

Preferably however R^4 is hydrogen.

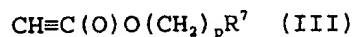
Preferably R^5 is a haloalkyl, and more preferably a
5 perhaloalkyl group, particularly a perfluoroalkyl group of
formula C_rF_{2r+1} where r is an integer of 1 or more, suitably
from 1-20, and preferably from 6-12 such as 8 or 10.

In a preferred embodiment, the compound of formula (I) is a
10 compound of formula (II)



where s is as defined above and R^7 is haloalkyl, in
15 particular a perhaloalkyl such as a C_{6-12} perfluoro group
like C_6F_{13} .

In an alternative preferred embodiment, the compound of
formula (I) is a compound of formula (III)
20



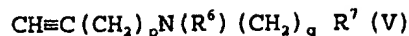
where p is an integer of from 1 to 20, and R^7 is as defined
above in relation to formula (II) above, in particular, a
25 group C_6F_{17} . Preferably in this case, p is an integer of
from 1 to 6, most preferably about 2.

Other examples of compounds of formula (I) are compounds of
formula (IV)



where p is as defined above, but in particular is 1, q is as
defined above but in particular is 1, and R^7 is as defined
in relation to formula (II), in particular a group C_6F_{13} ;

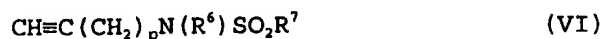
or compounds of formula (V)



where p is as defined above, but in particular is 1, q is as
5 defined above but in particular is 1, R⁶ is as defined above
an in particular is hydrogen, and R⁷ is as defined in
relation to formula (II), in particular a group C₇F₁₅;

or compounds of formula (VI)

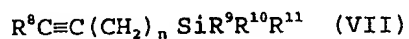
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where p is as defined above, but in particular is 1, R⁶ is as
defined above an in particular is ethyl, and R⁷ is as
15 defined in relation to formula (II), in particular a group
C₈F₁₇.

In an alternative embodiment, the alkyne monomer used in the
process of the invention is a compound of formula (VII)

20



where R⁸ is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl
optionally substituted by halo, R⁹, R¹⁰ and R¹¹ are
independently selected from alkyl or alkoxy, in particular
25 C₁₋₆ alkyl or alkoxy.

Preferred groups R⁸ are hydrogen or alkyl, in particular C₁₋₆
alkyl.

30 Preferred groups R⁹, R¹⁰ and R¹² are C₁₋₆ alkoxy in particular
ethoxy.

Using these compounds, coatings with water hydrophobicity
oleophobicity can be achieved.

Compounds of formula (I), (II), (III), (IV), (V), (VI) and (VII) are either known compounds or they can be prepared from known compounds using conventional methods.

5

Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by alternating current (AC) (e.g. radiofrequencies (Rf), microwaves) or direct current (DC). They may operate at atmospheric or sub-atmospheric pressures as are known in the art.

The plasma may comprise the monomeric compound alone, in the absence of other gases or in mixture with for example an inert gas. Plasmas consisting of monomeric compound alone may be achieved as illustrated hereinafter, by first evacuating the reactor vessel as far as possible, and then purging the reactor vessel with the organic compound for a period sufficient to ensure that the vessel is substantially free of other gases.

The surface coated in accordance with the invention may be of any solid substrate, such as fabric, metal, glass, ceramics, paper or polymers. In particular, the surface comprises a fabric substrate such as a cellulosic fabric, to which oil- and/or water-repellency is to be applied. Alternatively, the fabric may be a synthetic fabric such as an acrylic/nylon fabric.

The fabric may be untreated or it may have been subjected to earlier treatments. For example, it has been found that treatment in accordance with the invention can enhance the water repellency and confer a good oil-repellent finish onto

fabric which already has a silicone finish which is water repellent only.

Precise conditions under which the plasma polymerization
5 takes place in an effective manner will vary depending upon
factors such as the nature of the polymer, the substrate
etc. and will be determined using routine methods and/or the
techniques illustrated hereinafter. In general however,
polymerisation is suitably effected using vapours of
10 compounds of formula (I) at pressures of from 0.01 to 10
mbar, suitably at about 0.2mbar.

A glow discharge is then ignited by applying a high
frequency voltage, for example at 13.56MHz.

15

The applied fields are suitably of average power of up to
50W. Suitable pulsed fields are those which are applied in
a sequence which yields very low average powers, for example
of less than 10W and preferably of less than 1W. Examples
20 of such sequences are those in which the power is on for
20 μ s and off for from 10000 μ s to 20000 μ s.

The fields are suitably applied for a period sufficient to
give the desired coating. In general, this will be from 30
25 seconds to 3 hours, preferably from 2 to 30 minutes,
depending upon the nature of the monomer compound used and
the substrate etc.

Plasma polymerisation in accordance with the invention
30 particularly at low average powers has been found to result
in the deposition of highly fluorinated coatings which
exhibit very high levels of hydrophobicity.

In a preferred embodiment, the pulses are applied at a variable rate, with relatively long pulses applied, for example of from 1 to 10 secs on initially, reducing down to short pulses for example of from 100 μ s to 1 μ s on and 10 μ s to 5 1000 μ s off, later in the process. It is believed that such a regime leads to improved coatings because the initial long pulse leads to greater fragmentation of the monomer, leading to a more disorganised and therefore strongly bonding layer directly adjacent the substrate. Shorter late pulses means 10 that the upper layers deposited retain a more organised structure and so contain a greater number of long chains, which are responsible for the oil and water repellency on the surface.

15 Suitably the compound of formula (I) includes a perfluoroalkylated tail or moiety, in which case, the coating obtained by the process of the invention may have oleophobic as well as hydrophobic surface properties.

20 Thus the invention further provides a hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of a alkyl polymer and particularly a haloalkyl polymer which has been applied by the method described above. In particular, the substrates are fabrics but they 25 may be solid materials such as biomedical devices.

In a further aspect the invention provides the use of an optionally substituted alkyne or optionally substituted cycloalkyne having at least 5 carbon in the production of 30 water and/or oil repellent coatings by pulsed plasma deposition methods.

The invention will now be particularly described by way of example with reference to the accompanying diagrammatic drawings in which:

- 5 Figure 1 shows a diagram of the apparatus used to effect plasma deposition.

Example 1

Plasma Polymerisation of Alkyne

- 10 A fluorinated alkyne is placed into a monomer tube (1) (Fig. 1) and, if necessary, further purified using freeze-thaw cycles. Plasma polymerisation experiments can then be carried out in an inductively coupled cylindrical plasma reactor vessel (2) of 5cm diameter, 470cm³ volume, base
15 pressure of 7×10^{-3} mbar, and with a leak rate of better than 2×10^{-3} cm³min⁻¹. The reactor vessel (2) is connected by way of a "viton" O-ring (3), a gas inlet (4) and a needle valve (5) to the monomer tube (1).
- 20 A thermocouple pressure gauge (6) is connected by way of a Young's tap (7) to the reactor vessel (2). A further Young's tap (8) connected with an air supply and a third (9) lead to an E2M2 two stage Edwards rotary pump (not shown) by
25 way of a liquid nitrogen cold trap (10). All connections are grease free.

- An L-C matching unit (11) and a power meter (12) is used to couple the output of a 13.56 Mhz R.F. generator (13), which
30 is connected to a power supply (14), to copper coils (15) surrounding the reactor vessel (2). This arrangement ensures that the standing wave ratio (SWR) of the transmitted power to partially ionised gas in the reactor vessel (2) can be minimised. For pulsed plasma deposition,

a pulsed signal generator (16) can be used to trigger the R.F power supply, and a cathode ray oscilloscope (17) is used to monitor the pulse width and amplitude. The average power $\langle P \rangle$ delivered to the system during pulsing is given by
5 the following formula:

$$\langle P \rangle = P_{cw} \{ T_{on} / (T_{on} + T_{off}) \}$$

where $T_{on} / (T_{on} + T_{off})$ is defined as the duty cycle and P_{cw} is
10 the average continuous wave power.

In order to carry out polymerization/deposition reactions the reactor vessel (2) was cleaned by soaking overnight in a chlorox bleach bath, then scrubbing with detergent and
15 finally rinsing with isopropyl alcohol followed by oven drying. The reactor vessel (2) is then incorporated into the assembly as shown in Figure 1 and further cleaned with a 50W air plasma for 30 minutes. Next the reactor (2) vessel is vented to air and the substrate to be coated (19) is
20 placed in the centre of the chamber defined by the reactor vessel (2) on a glass plate (18). The chamber is then evacuated back down to base pressure (7.2×10^{-3} mbar).

25 Monomeric vapour is then introduced into the reaction chamber at a constant pressure of ~0.2mbar and allowed to purge the plasma reactor, followed by ignition of the glow discharge. Typically 2-15 minutes deposition time can be used, and should be sufficient to give complete coverage of
30 the substrate. After this, the R.F generator is switched off and the vapour allowed to continue to pass over the substrate for a further 5 minutes before evacuating the reactor back down to base pressure, and finally venting up to atmospheric pressure.

The deposited plasma polymer coatings can be characterised immediately after deposition by X-ray photoelectron spectroscopy (XPS). Complete plasma polymer coverage is confirmed by the absence of any Si (2p) XPS signals showing through from the underlying glass substrate.

A control experiment, where the vapour is allowed to pass over the substrate for 15 minutes and then pumped down to base pressure can be carried out. If the results of the control show the presence of a large Si (2p) XPS signal from the substrate, it can be concluded that the coatings obtained during plasma polymerisation are not just due to absorption of the monomer onto the substrate.

The experiments are preferably carried out with average powers in the range of from 0.01 to 50W, for example from 0.3 to 50W.

Example 2

Oil and Water Repellency Test

Once a substrate such as cotton, has been subjected to deposition conditions as described in Example 1, they may then be for wettability using "3M Test Methods" (3M oil repellency Test 1, 3M Test Methods Oct.1, 1988). As a Water repellency test, the 3M water repellency Test II, water/alcohol drop test, 3M Test 1, 3M Test Methods, October 1, 1988 is suitable. These tests are designed to detect a fluorochemical finish on all types of fabrics by measuring:

- (a) aqueous stain resistance using mixtures of water and isopropyl alcohol.

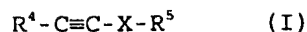
(b) the fabric's resistance to wetting by a selected series of hydrocarbon liquids of different surface tensions.

5 These tests are not intended to give an absolute measure of the fabric's resistance to staining by watery or oily materials, since other factors such as fabric construction, fibre type, dyes, other finishing agents, etc., also influence stain resistance. These tests can, however, be
10 used to compare various finishes. The water repellency tests comprises placing 3 drops of a standard test liquid consisting of specified proportions of water and isopropyl alcohol by volume onto the plasma polymerised surface. The surface is considered to repel this liquid if after 10
15 seconds, 2 of the 3 drops do not wet the fabric. From this, the water repellency rating is taken as being the test liquid with the greater proportion of isopropyl alcohol which passes the test. In the case of the oil repellency test, 3 drops of hydrocarbon liquid are placed on the coated
20 surface. If after 30 seconds no penetration or wetting of the fabric at the liquid-fabric interface occurs around 2 of the 3 drops is evident, then the test is passed.

The oil repellency rating is taken to be the highest-
25 numbered test liquid which does not wet the fabric surface (where the increasing number corresponds to decreasing hydrocarbon chain and surface tension).

Claims

1. A method of coating a surface with a polymer layer,
5 which method comprises exposing said surface to a plasma comprising an optionally substituted alkyne containing monomer so as to form an oil or water repellent coating on said substrate.
- 10 2. A method according to claim 1 wherein the optionally substituted alkyne containing monomer comprises chain of carbon atoms which include one or more carbon-carbon triple bonds and may be optionally interposed with a heteroatom.
- 15 3. A method according to claim 1 or claim 2 wherein the alkyne is optionally substituted by halo, cyano, nitro, oxo, epoxide, optionally substituted cycloalkyl, optionally substituted aryl, optionally substituted aralkyl, optionally substituted heterocyclyl, $C(O)_nR^1$, OR^1 , $S(O)_mR^1$, NR^2R^3 ,
20 $C(O)NR^2R^3$, $OC(O)NR^2R^3$, $=NOR^2$, $-NR^2C(O)_nR^3$, $-NR^1CONR^2R^3$, $-N=CR^2R^3$, $S(O)_mNR^2R^3$ or $-NR^2S(O)_mR^1$ where R^1 , R^2 and R^3 are independently selected from hydrogen or alkyl, aralkyl, cycloalkyl, aryl or heterocyclyl, any of which may be optionally substituted, or R^2 and R^3 together form an optionally substituted ring
25 which optionally contains further heteroatoms such as sulphur, oxygen and nitrogen, n is an integer of 1 or 2, m is 0 or 1 or 2.
4. A method according to any one of the preceding claims
30 wherein the optional substituents comprise halogen.
5. A method according to any one of the preceding claims wherein the alkyne containing monomer is a compound of formula (I)

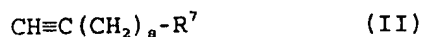


where R^4 is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl
 5 optionally substituted by halo;
 X is a bond or a bridging group; and
 R^5 is an alkyl, cycloalkyl or aryl group optionally
 substituted by halogen.

10 6. A method according to claim 5 wherein the bridging
 group X comprises a group of formula
 $-(CH_2)_s-$, $-CO_2(CH_2)_p-$, $-(CH_2)_pO(CH_2)_q-$, $-(CH_2)_pN(R^6)CH_2)_q-$,
 $-(CH_2)_pN(R^6)SO_2-$, where s is 0 or an integer of from 1 to 20,
 p and q are independently selected from integers of from 1
 15 to 20; and R^6 is hydrogen, alkyl, cycloalkyl or aryl.

7. A method according to claim 5 or claim 6 wherein R^4 is
 hydrogen.

20 8. A method according to claim 7 wherein the compound of
 formula (I) is a compound of formula (II)



25 where s is as defined in claim 6 and R^7 is haloalkyl.

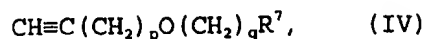
9. A method according to claim 7 wherein the compound of
 formula (I) is a compound of formula (III)



where p is an integer of from 1 to 20, and R^7 is as defined
 in claim 8.

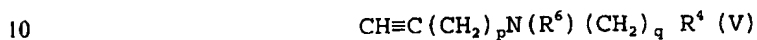
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10. A method according to claim 7 wherein the compound of formula (I) is a compound of formula (IV)



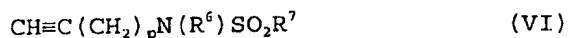
where p and q are as defined in claim 6, and R⁷ is as
5 defined in claim 8.

11. A method according to claim 7 wherein the compound of formula (I) is a compound of formula (V)



where p and q are as defined in claim 6, R⁶ is as defined in claim 6 and R⁷ is as defined in claim 8.

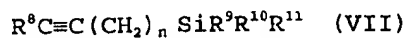
12. A method according to claim 7 wherein the compound of
15 formula (I) is a compound of formula (VI)



where p is as defined in claim 6 and R⁷ is as defined in claim 8.

20

13. A method according to any one of claims 1 to 4 wherein the alkyne containing monomer is a compound of formula (VII)



25 where R⁸ is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl optionally substituted by halo, R⁹, R¹⁰ and R¹¹ are independently selected from alkyl or alkoxy.

14. A method according to any one of the preceding claims
30 wherein the surface is a surface of a fabric, metal, glass, ceramics, paper or polymer substrate.

15. A method according to claim 14 wherein the substrate is a fabric.

16. A method according to any one of the preceding claims wherein the plasma is generated by an alternating current voltage.

5

17. A method according to claim 16 wherein the alternating current voltage is produced by radio frequencies or microwaves.

10 18. A method according to any one of claims 1 to 15 wherein the plasma is produced by direct current voltage.

19. A method according to any one of the preceding claims wherein the gas pressure of the organic compound is from
15 0.01 to 10 mbar.

20. A method according to anyone of claims 1 to 18 wherein the plasma is operated at atmospheric pressure.

20 21. A method according to any one of the preceding claims wherein a glow discharge is ignited by applying a high frequency voltage.

22. A method according to claim 21 wherein the voltage is
25 applied as a continuous field.

23. A method according to claim 21 wherein the voltage is applied as a pulsed field.

30 24. A method according to claim 23 wherein pulses are applied in a sequence which yields low average power.

26. A method according to any one of the preceding claims wherein the plasma polymerisation takes place for from 2 to 15 minutes.

5

27. A hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of a polymer which has been applied by the method according to any one of claims 1 to 26.

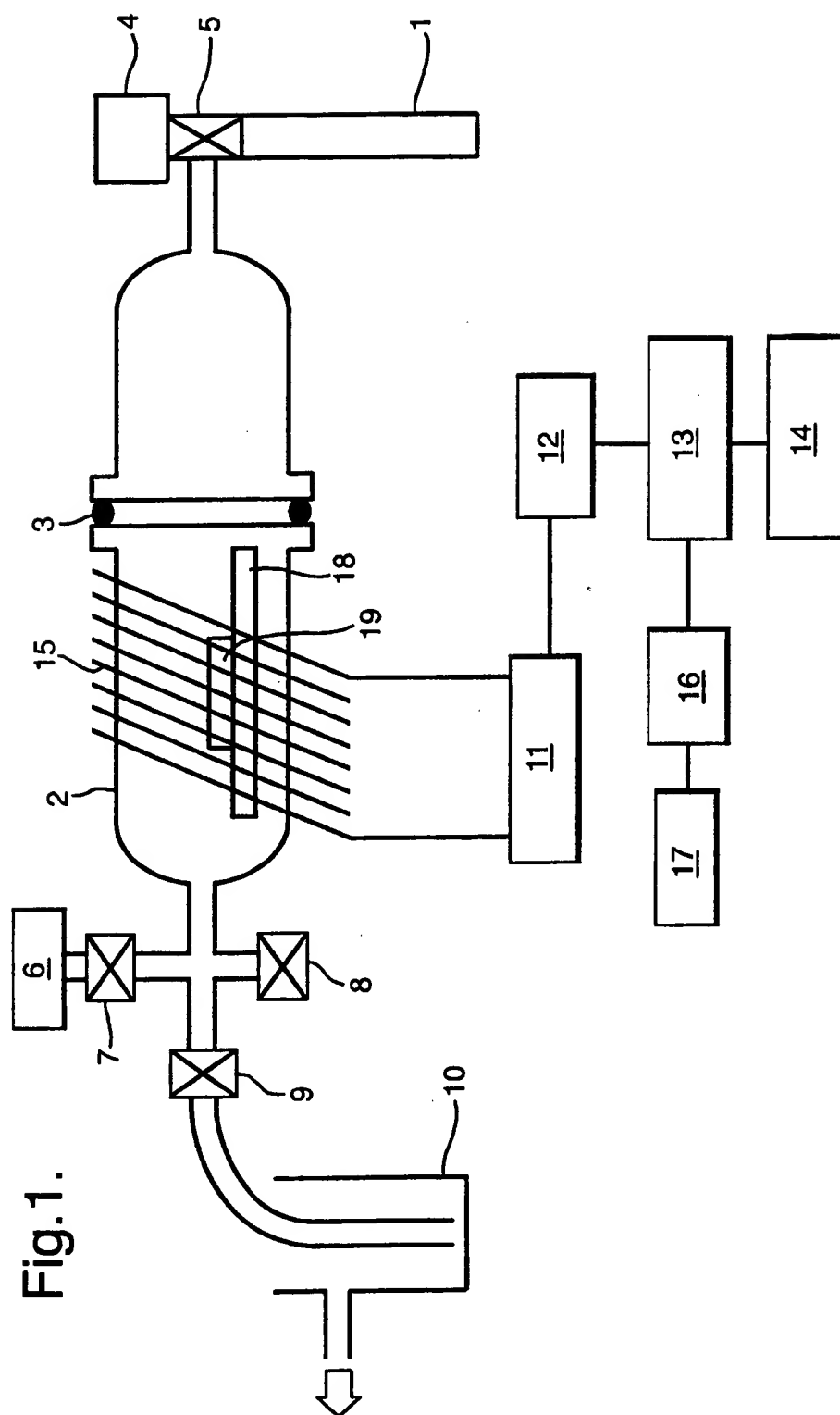
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28. A hydrophobic or oleophobic substrate according to claim 27 wherein the polymer is a haloalkyl polymer.

29. A substrate according to claim 27 or claim 28 which is a fabric.

15

30. An item of clothing which comprises a fabric according to claim 29.



INTERNATIONAL SEARCH REPORT

Int. l. Application No
PCT/GB 99/03224

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B05D7/24 D06M10/02 D06M14/18 D06M10/08 D06M10/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B05D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 345 (C-0864), 3 September 1991 (1991-09-03) & JP 03 134034 A (CENTRAL GLASS CO LTD), 7 June 1991 (1991-06-07) abstract	1,2,14, 27
X	DATABASE WPI Section Ch, Week 198714 Derwent Publications Ltd., London, GB; Class A89, AN 1987-098131 XP002127946 & JP 62 046685 A (CANON KK), 28 February 1987 (1987-02-28) abstract	1-3,14, 27



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

18 January 2000

Date of mailing of the international search report

27/01/2000

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INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/GB 99/03224

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P, X	EP 0 896 035 A (UNIV TEXAS) 10 February 1999 (1999-02-10) page 8, line 45 -page 10, line 36; claims ----	1-4, 14, 16-26
X	YOSHIMURA K ET AL: "PREPARATION OF HYDROPHILIC PLASMA-POLYMERS DERIVED FROM OXYGEN- CONTAINING ORGANIC MONOMERS" JOURNAL OF APPLIED POLYMER SCIENCE, US; JOHN WILEY AND SONS INC. NEW YORK, vol. 59, no. 6, 7 February 1996 (1996-02-07), page 1033-1042 XP000551855 ISSN: 0021-8995 the whole document ----	1-3, 14, 16, 17, 19, 21
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International Application No

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